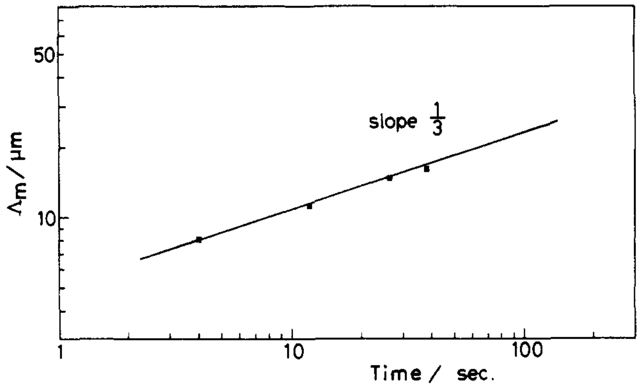

Figure 4. Logarithmic plot of the correlation length Λ_m vs. time spent for the isothermal phase separation of X-7G/PET (50/50) mixture film at 256 °C.

crystalline networks. Detailed analyses on the scattering patterns will be described elsewhere.[28]

Figure 4 shows the time evolution of the correlation length Λ_m's during isothermal phase separation at 256 °C. Λ_m's were measured by image processing of the optical microscopic pictures obtained in the late stage of the unmixing so that the network structure could be unequivocally distinguished with the dynamic image analyzer built in our laboratory.[33] Details of the dynamic image analyzer[33] and the method of extracting Λ_m's will be reported elsewhere.[28] Preliminary experimental results show the power law

$$\Lambda_m \sim t^{1/3} \qquad (1)$$

The $^1/_3$-power law is the one familiar for the droplet growth caused by the hydrodynamic effect[16,17,34] or by the Lifshitz–Slyozov process.[15] The growth of the droplets occurs as a consequence of their diffusion and coalescence so that

$$R^2(t) \sim D(t)t \qquad (2)$$

where $R(t)$ is the size of the droplet and $D(t)$ is time-dependent diffusivity of the droplet, which, in turn, is given by

$$D(t) \sim k_BT/\eta R(t) \qquad (3)$$

where k_BT is the thermal energy and η is the viscosity. From eq 2 and 3 one obtains the $^1/_3$-power law

$$\Lambda_m \sim R(t) \sim (k_BT/\eta)^{1/3}t^{1/3} \qquad (4)$$

Needless to say, further investigation is required as to whether the $^1/_3$-power law observed in the preliminary study of the unmixing dynamics of the liquid crystalline component and isotropic liquid component exactly corresponds to the $^1/_3$-power law in the growth of patterns caused by hydrodynamic interactions of the Lifshitz–Slyozov process found for the isotropic liquid or solid mixtures. Moreover, the $^1/_3$-power law itself has to be further investigated over a much wider time scale and temperature range. Further work along this line is currently in progress in our laboratory. However, all evidence presented in this paper indicates that spinodal decomposition and subsequent coarsening processes similar to those for isotropic liquids and solids occur even when one component is a liquid crystalline polymer and forms a liquid crystal phase.

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(41) Wide-angle X-ray diffraction and small-angle X-ray scattering showed the melting point of the pure PET is close to 275 °C, slightly higher than 256 °C. However, the crystallinity of the PET homopolymer in the mixture, if it existed, appears to make an insignificant contribution to the anisotropy of the PET-rich phase.

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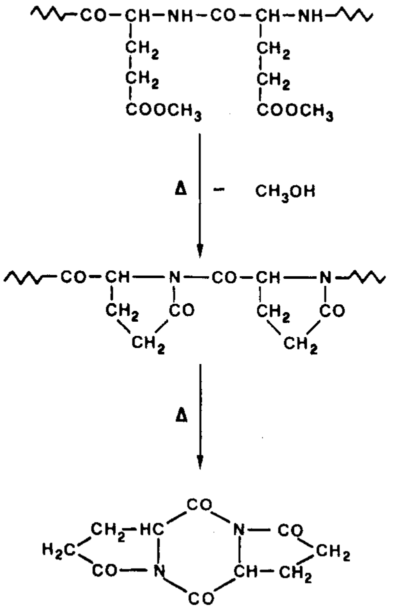
Comments on the Paper "Thermal Decomposition of Poly(γ-methyl L-glutamate)"

A paper dealing with the pyrolysis–gas chromatography–mass spectrometry (GC–MS) of poly(γ-methyl L-glutamate) (PMLG) appeared recently in this journal.[1] Pyrolysis products of up to m/z 85 were eluted from the GC column and identified by MS.

On the basis of these results, it was concluded that the primary decomposition products evolving from PMLG are methanol, carbon dioxide, methane, and some other gaseous materials.[1]

Scheme I

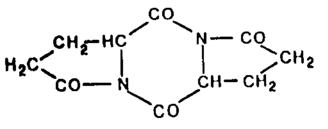


I

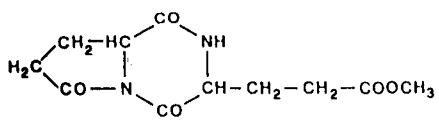
The authors were, apparently, unaware of our recent results[2] on the thermal decomposition of PMLG, investigated by direct pyrolysis–mass spectrometry (DP–MS).

In the DP–MS technique,[2] polymers are introduced via a direct insertion probe and the temperature is increased gradually to a point at which thermal decomposition reactions occur; the volatile products formed are then ionized and detected.

Two diketopiperazines (I and II) were detected, together with methanol, among the pyrolysis products of PMLG.[2]



I



II

These findings gave us a firm basis so as to propose[2] a primary thermal fragmentation mechanism for PMLG (Scheme I).

In fact, one of the advantages of the DP–MS technique is that the pyrolysis is accomplished under a high vacuum and, therefore, that the thermal products formed are volatilized and removed readily from the hot zone. This, together with the low probability of molecular collision and the fast detection, reduces, to a large extent, the occurrence of secondary reactions. Consequently, the thermal fragments detected are due almost exclusively to primary reactions. The information thus obtained is, therefore, of particular importance in order to assess the primary thermal decomposition mechanism of a particular polymer.[2]

Secondary and/or tertiary decomposition reactions cannot be avoided by using pyrolysis–GC–MS, since the pyrolysis is performed at atmospheric pressure and the pyrolysis products are kept for some time in the GC column at a high temperature.

In view of our previous DP–MS results,[2] the pyrolysis products of PMLG which were detected by pyrolysis–GC–MS in ref 1 appear to be smaller, secondary, products. It is difficult to derive a mechanism of primary thermal decomposition of PMLG from this kind of information (see Scheme I).

Rather, it should be realized that pyrolysis–GC–MS experiments are actually concerned with the thermal decomposition of diketopiperazines I and II, which are, themselves, the primary pyrolysis products originating from PMLG.

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Registry No. I, 14612-22-7; II, 104807-55-8; PMLG (homopolymer), 25086-16-2; PMLG (SRU), 25036-43-5.

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Trialkylsilyl Triflates, Novel Initiators for Cationic Polymerization

We wish to report that trialkylsilyl trifluoromethanesulfonates are highly effective novel initiators for the cationic polymerization of vinyl monomers and oxacyclic compounds.

Trialkylsilyl trifluoromethanesulfonates (triflates) have enjoyed wide use as electrophilic reagents in organic chemistry.[1-5] They are highly reactive toward electron-rich olefins and to carbonyl and oxacyclic compounds. Nevertheless recent authoritative reviews[6-10] contain no mention of their use as initiators for the cationic polymerization of such monomers.

Representative results for the initiation of the cationic polymerization of some common electron-rich monomers, using trimethylsilyl triflate (**1**) and triisopropylsilyl triflate (**2**), are given in Table I. Careful purification of reagents ensured that triflic acid was not responsible for these polymerizations. The polymerizations proceed rapidly at

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